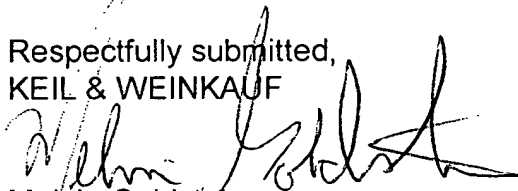


REMARKS

Claims 1-4 and 9 have been canceled. The present application is directed to non-elected claims 5-7 of the parent application. Favorable action on the application by the examiner is solicited.

Please charge any shortage in fees due in connection with the filing of this paper, including Extension of Time fees to Deposit Account No. 11-0345. Please credit any excess fees to such deposit account.

Respectfully submitted,  
KEIL & WEINKAUF

  
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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**  
**IN THE SPECIFICATION**

Page 1, after the title, insert:

-- This is a divisional application of Serial No. 09/303,600, filed on May 3, 1999.--

**IN THE CLAIMS**

Cancel claims 1-4 and 8.

Amend claims 5 and 7 as follows:

5. (amended) A process for producing large polyethylene blow moldings [as claimed in claim 1] having a bursting strength determined by a drop height test at 18°C of more than 3 m by forming polyethylene of density  $\rho \geq 0.94 \text{ g/cm}^3$ , of melt flow rate MFR  $190/21.6 < 60 \text{ g/10 min}$  and of notched tensile impact strength  $a_{zK} (-30^\circ\text{C})$  not less than  $250 \text{ kJ/m}^2$ , [forming the same] at high temperatures to give a large blow molding, and allowing the large blow molding to cool to room temperature, [which comprises] and, in a further step, annealing the large blow molding at from 60 to  $135^\circ\text{C}$  until the notched tensile impact strength  $a_{zK} (-30^\circ\text{C})$ , measured in accordance with ISO 8256, is at least  $300 \text{ kJ/m}^2$ , and then cooling the same again to room temperature.

7. (amended) A process as claimed in claim 5 [or 6], wherein the large blow molding is formed by extrusion blow molding.

**COPY OF ALL CLAIMS**

5. (amended) A process for producing large polyethylene blow moldings having a bursting strength determined by a drop height test at 18°C of more than 3 m by forming polyethylene of density  $\rho \geq 0.94 \text{ g/cm}^3$ , of melt flow rate  $\text{MFR } 190/21.6 < 60 \text{ g/10 min}$  and of notched tensile impact strength  $a_{zK} (-30^\circ\text{C})$  not less than  $250 \text{ kJ/m}^2$ , at high temperatures to give a large blow molding, and allowing the large blow molding to cool to room temperature, and, in a further step, annealing the large blow molding at from 60 to 135°C until the notched tensile impact strength  $a_{zK} (-30^\circ\text{C})$ , measured in accordance with ISO 8256, is at least  $300 \text{ kJ/m}^2$ , and then cooling the same again to room temperature.

6. A process as claimed in claim 5, wherein the polyethylene used has a weight-average molar mass  $M_w$  of from 200 to 800 kg/mol and a breadth of molar mass distribution  $M_w/M_n$  of from 5 to 80.

7. (amended) A process as claimed in claim 5, wherein the large blow molding is formed by extrusion blow molding.

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SN 10/035,103

# Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 20:

Photography to Plastics, Processing

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz



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Production Director: Maximilian Montkowski  
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Library of Congress Card No. 84-25-829

Deutsche Bibliothek, Cataloguing-in-Publication Data:

**Ullmann's encyclopedia of industrial chemistry** / ed.: Barbara Elvers ... [Ed. advisory board Hans-Jürgen Arpe ...]. — Weinheim ; Basel (Switzerland) ; Cambridge ; New York, NY : VCH.

Teilw. executive ed.: Wolfgang Gerhartz

Bis 4. Aufl. u. d. T.: Ullmanns Encyklopädie der technischen Chemie

NE: Gerhartz, Wolfgang [Hrsg.]; Elvers, Barbara [Hrsg.]; Encyclopedia of industrial chemistry

Vol. A. Alphabetically arranged articles.

20. Photography to plastics, processing. — 5. completely rev. ed. — 1992

ISBN 3-527-20120-3 (Weinheim ...)

ISBN 0-89573-170-3 (New York)

#### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

© VCH Verlagsgesellschaft mbH, D-6940 Weinheim (Federal Republic of Germany), 1992.

Printed on acid-free paper

#### **Distribution**

VCH Verlagsgesellschaft, P.O. Box 10 11 61, D-6940 Weinheim (Federal Republic of Germany)

Switzerland: VCH Verlags-AG, P.O. Box, CH-4020 Basel (Switzerland)

Great Britain and Ireland: VCH Publishers (UK) Ltd., 8 Wellington Court, Wellington Street, Cambridge

CB1 1HZ (Great Britain)

USA and Canada: VCH Publishers, 220 East 23rd Street, New York NY 10010-4606 (USA)

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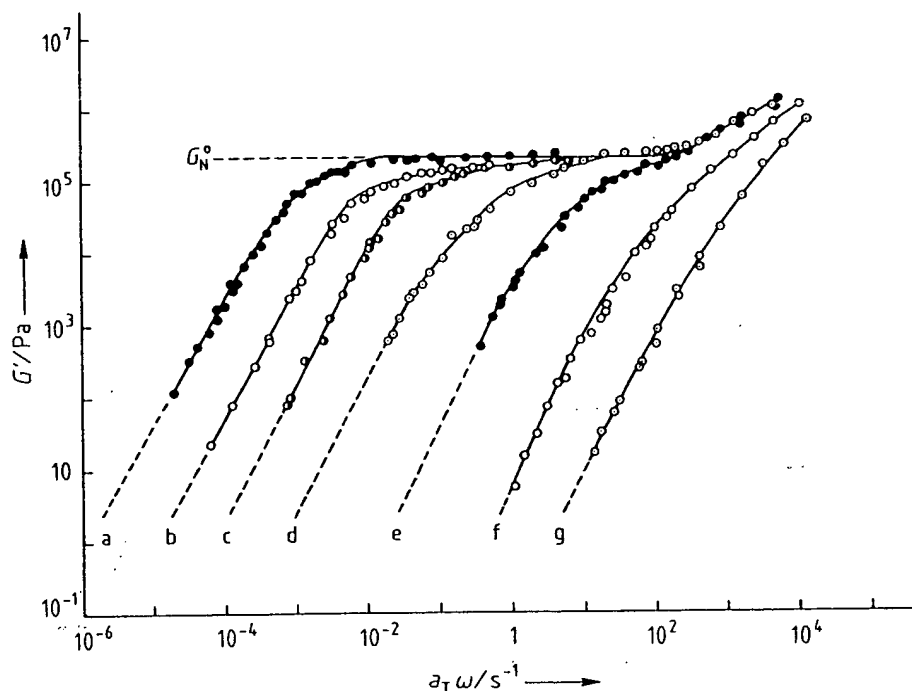
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Cover design: Wolfgang Schmidt

Composition, printing, and bookbinding: Graphischer Betrieb Konrad Triltsch, D-8700 Würzburg

Printed in the Federal Republic of Germany



**Figure 50.** Frequency dependence of the shear storage modulus  $G'$  for narrow-distribution polystyrene melts of different molar masses  $M$ . A shift factor  $a_T$  was used to convert to 160°C data measured at various temperatures  
 a)  $M = 581\,000$  g/mol; b)  $M = 351\,000$  g/mol; c)  $M = 215\,000$  g/mol; d)  $M = 113\,000$  g/mol; e)  $M = 46\,900$  g/mol; f)  $M = 14\,800$  g/mol; g)  $M = 8\,900$  g/mol

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The end ranges of these spectra are molar mass dependent; this behavior must come from long-range conformational changes. Since the transition range characterizes viscous behavior, and the end range viscoelastic behavior, the plateau range must reflect rubbery behavior (see Fig. 47 for the temperature dependence).

The *rubbery behavior* of polymer melts can be described by the theories of entropy elasticity according to which the shear modulus of chemically cross-linked polymers depends on the molar concentration of network junctions. The plateau modulus  $G_N^0$  of melts thus indicates the concentration of temporary junctions (entanglements). The molar mass  $M_e$  of segments between such junctions of polymers with volume fractions  $\phi_p$  in solution ( $\phi_p = 1$  for melts) and polymer melt densities  $\rho_p$  is given by

$$M_e = RT \cdot \rho_p \cdot \phi_p / G_N^0 \quad (90)$$

These dynamic entanglement molar masses  $M_e$  are a factor  $2.0 \pm 0.2$  lower than the corresponding molar masses  $M_c$  from rest viscosities (Table 24).

The plateau is not well developed or may even be absent for polymers with broad molar

**Table 24.** Critical molar masses for entanglement from shear moduli ( $M_e$ ) and rest viscosities ( $M_c$ )

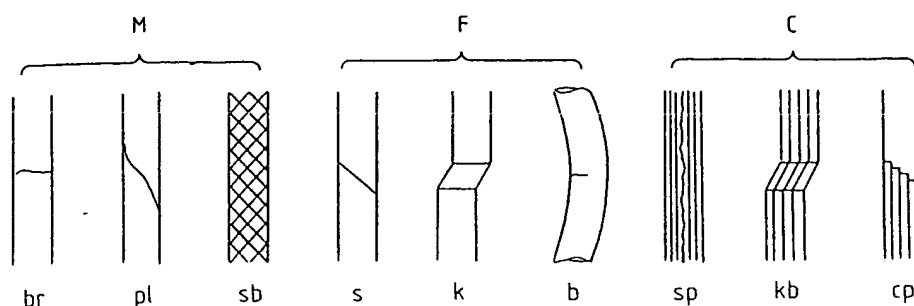
Polymer	T °C	$M_c$ g/mol	$M_e$ g/mol	$\frac{M_c}{M_e}$
Polyethylene	190	3800	1790	2.1
Polypropylene, it	190	7000		
Polyisobutylene	25	15200	8800	1.7
Polydimethylsiloxane	25	24500	10500	2.4
Poly(vinyl acetate), at	57	24500	12000	2.0
Poly( $\alpha$ -methylstyrene), at	100	28000	13500	2.1
Polystyrene, at	190	35000	18100	1.9

mass distributions; a complicated dependence of shear compliances on higher molar mass averages has been predicted by reptation theory.

## 8.6. Fracture

### 8.6.1. Overview

Polymers break very differently depending on their chemical and physical structure; environment (humidity, solvents, temperature); and the type, duration, and frequency of deforma-



**Figure 51.** Failure modes of polymers (matrix M), fibers (F), and fiber-reinforced polymer composites (C) by brittle failure (br), plastic flow (pl), shear band formation (sb), shearing (s), kink formation (k), bending (b), longitudinal splicing (sp), formation of kink bands (kb), and step formation by compression (cp)

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tion. Some polymers break immediately; others are unchanged even after months. The fracture surface can be smooth or splintery; the elongation at fracture, less than 1% or greater than 1000%.

Two fracture modes can be distinguished: brittle and tough (ductile). Brittle polymers fracture perpendicularly to the stress direction, tough polymers longitudinally (Fig. 51). A polymer is defined as brittle if its elongation at break is less than 20%.

*Brittle fractures* are rare for ideal solids since many bonds must be severed simultaneously. Real polymers however contain many small imperfect regions that act as "nuclei" for the formation of microcracks. Brittle polymers usually possess "natural" microvoids, which may also appear in drawn amorphous polymers or through separation of crystal lamellae in hard-tough polymers.

*Tough failures* (ductile fractures) are caused by viscous flow ("plastic flow"). This process may involve the slipping of chain segments past each other (amorphous polymers) or the movement of crystalline domains (partly crystalline polymers). Polymer chains may also de-entangle at long times and under small stresses. The same processes and additional ones may occur on failure of composites (Fig. 51).

Polymers are subjected to very different stress conditions in typical applications; they thus experience different failure modes. Test methods try to simulate complex real-life situations by standardized procedures. They include long-term experiments such as static deformations under constant load by tension, compression, or bending; short-term methods such as tensile tests under various speeds or impact tests with unnotched or notched specimens; dynamic testing with variation of the number of loadings—unloadings, impacts, vibrations, etc.

### 8.6.2. Theoretical Fracture Strength

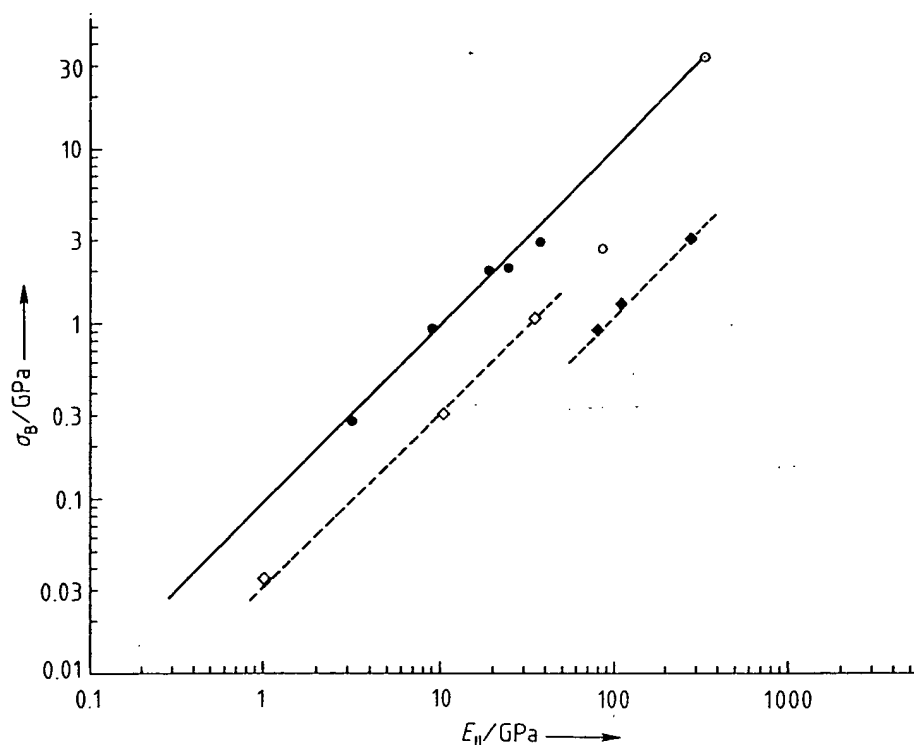
The fracture of brittle polymers generates free radicals. Since the probabilities of such homolyses depend on bond strengths, which also determine tensile moduli, relationships must exist between the theoretical moduli and the theoretical fracture strengths of polymers.

Bonds are severed if atoms are separated from each other by certain distances  $L_b$  greater than their equilibrium distances  $L_o$ . The necessary theoretical strength  $\sigma_{||}^o$  is given by [5]

$$\sigma_{||}^o = \frac{E_{||}^o \cdot (L_b - L_o)}{\pi L_o} = K \cdot E_{||}^o \quad (91)$$

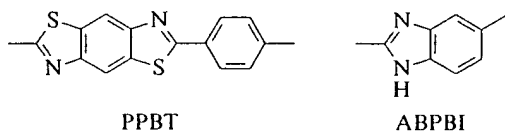
Polymer main-chain bonds break at approximately the same relative distance ( $L_b \approx 1.3 L_o$ ) because bond lengths and strengths are not too different for bonds such as C—C, C—O, and C—N. Thus,  $K \approx 0.095$  and the theoretical fracture strength  $\sigma_{||}^o$  should be ca. one-tenth of the theoretical tensile modulus  $E_{||}^o$  in the chain direction, regardless of the chemical nature of the polymer. Polyethylene with a theoretical modulus of 340 GPa (Table 21) should thus have a theoretical fracture strength of ca. 32 GPa [i.e., much higher than the theoretical strength of steel (ca. 20 GPa)]. Industrially manufactured ultradrawn polyethylene fibers have higher experimental fracture strengths than steel (2.9 GPa = 2.7 N/tex vs. 2.5 GPa).

The theoretical fracture strength–tensile modulus relationship of Equation (91) has been realized for certain ultradrawn polyethylenes in which both the predicted proportionality constant  $K = 0.095$  and the first power of  $E$  were found (Fig. 52). The type of same relationship is also observed for molecular composites of poly (*p*-phenylene-2,6-bisbenzthiazole) (PPBT) with



**Figure 52.** Tensile strength at break as function of tensile modulus: (●) experimentally ultradrawn ultra-high-modulus polyethylenes; (○) industrially manufactured ultradrawn polyethylene (Dyneema); (◊) theory for perfectly aligned polyethylene; (◊) heterogeneous molecular composites of ABPBI fibers or PBT fibers or films in ABPBI matrix; (◆) homogeneous molecular composites of PBT fibers or PBT fibers for films in ABPBI. Solid line corresponds to  $\sigma_B = 0.095 \cdot E_{||}$

rodlike mesogens in coillike polybenzimidazole (ABPBI), albeit with a lower proportionality constant. In other ultradrawing experiments, a power dependence  $\sigma = K' \cdot E^n$  was found, however.



### 8.6.3. Real Fracture Strength

The lower than theoretical fracture strengths of most polymers (see Tables 21 and 22) are caused by many factors. Theoretical fracture strengths relate to infinitely long, completely aligned, immobile polymer chains. End groups and chain folds act as disturbances: fracture strengths of conventional polymers increase with increasing molar mass and become practically constant above a "critical" molar mass.

At the latter molar mass range, chain segments of amorphous polymers are distributed at random. A brittle fracture across such polymers

will create two new surfaces with a total surface energy of  $2 \gamma_{iv}$ . The theoretical fracture strength for brittle, energy-elastic bodies

$$\sigma_a^0 = (E \cdot \gamma_{iv} / L_0)^{1/2} \quad (92)$$

now depends on the product of modulus and surface energy (Ingles theory). The Ingles theory works well for silicate glasses.

The experimentally found fracture strengths  $\sigma_b$  of plastics are however much lower than the strengths predicted by Equation (92). The ratios  $\sigma_a^0 / \sigma_{exp}$  of molded (unoriented) plastics decrease with increasing elongation  $\epsilon_b$  at break (Fig. 53), whereas those of drawn fibers (partially oriented chain segments) increase.

The reason for the lower than expected fracture strengths of amorphous polymers is the presence of microvoids, which act on drawing as nuclei for cracks. According to the Griffith theory, a crack can grow only if the energy required for the fracture of chemical bonds is just surpassed by the stored elastic energy. This theory predicts a dependence of the fracture strength on crack length  $L$ :

$$\sigma_B = [(2 E \cdot \gamma_{iv}) / (\pi \cdot L)]^{1/2} \quad (93)$$



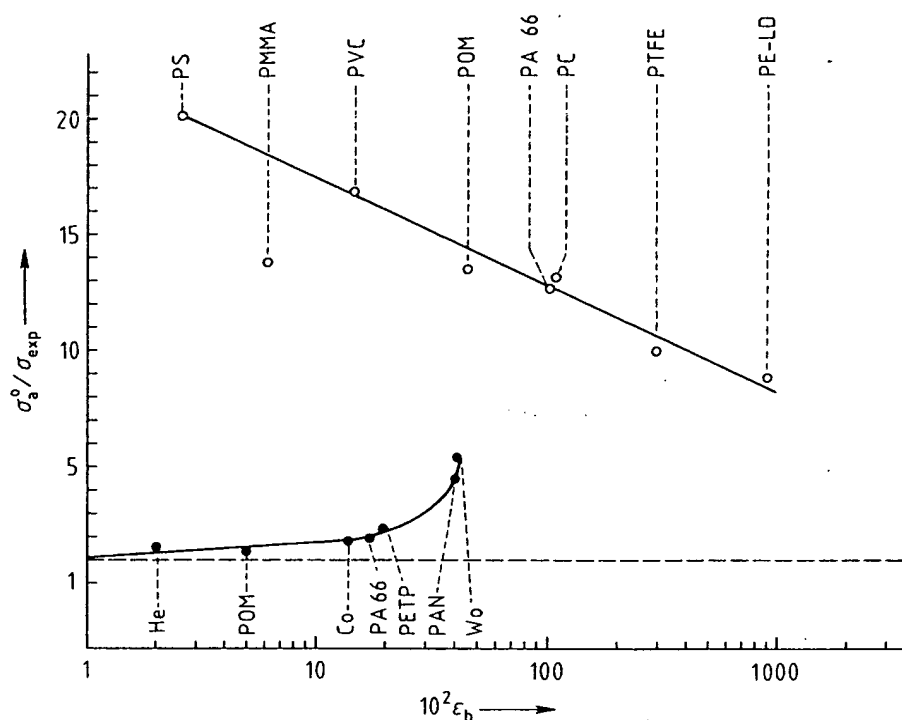


Figure 53. Ratio  $\sigma_a^0/\sigma_{exp}$  of theoretical [Eq. (92)] and experimental fracture strengths as function of elongation at break  $\epsilon_b$  for (o) nonoriented (molded plastics) and (●) oriented (fibers) polymers  
He = hemp, Co = cotton, Wo = wool (for other abbreviations see Table 1)

This functionality is indeed observed for artificially introduced long cracks. The predicted fracture strengths are however much lower than those found by experiment. Furthermore, deviations from Equation (93) occur at small crack lengths because the fracture behavior of plastics is not dominated by the cleavage of chemical bonds but by other types of energy absorption (crazing; shear flow).

On drawing, stresses are imposed on microvoids. The polymer reaches its upper yield stress at sufficiently high stress concentrations at the tip of such a void and relieves the stress by stress softening (Fig. 44). The induced cooperative movements of chain segments cause long-range changes of macroconformations. In partially crystalline polymers, these changes can occur only in amorphous domains; spherulitic polymers break accordingly either between spherulites or in the radial spherulite direction.

The cooperative movements of segments lead to either shear or normal stress yielding. On shearing, the whole specimen yields either homogeneously or heterogeneously (localized). In the latter case, shear bands are formed at angles of  $38-45^\circ$  to the stress direction (Fig. 51). Chain segments are arranged at angles between shear bands and stress directions.

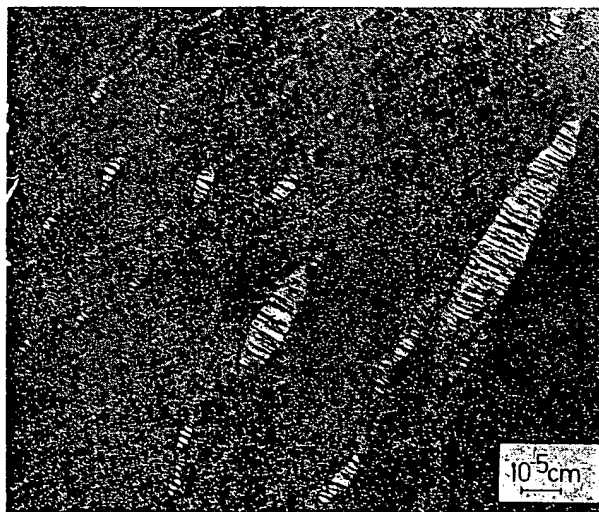


Figure 54. Crazes in a polystyrene drawn to 25% [78]

All polymers with upper yield values form crazes upon stress softening (Fig. 54), regardless of whether they are amorphous, crystalline, linear, or cross-linked. Crazes can be up to  $100\text{ }\mu\text{m}$  long and  $10\text{ }\mu\text{m}$  wide; their long axes are parallel to the stress direction. They are not voids since their interior is filled with amorphous microfibrils of  $0.6-30\text{ nm}$  diameter; these microfibrils are oriented in the stress direction (i.e.,

perpendicular to the craze long axes). On further deformation, microvoids are formed.

The formation of crazes is the primary mechanism for the dissipation of stress energy. It is utilized in the rubber reinforcement of polystyrene. Rubber-modified polypropylene, on the other hand, deforms mainly by shear flow.

#### 8.6.4. Impact Resistance

Impact strength is the resistance of a material to impact. It is one of the many quantities used to characterize the strength of a material under (the usually complex) use conditions; all test methods are thus standardized. Most test methods measure the energy required to break a notched or unnotched specimen (Izod, Charpy, high-speed tensile). Impact speeds range from  $10^{-5}$ – $10^{-1}$  m/s in conventional tensile tests to 20–240 m/s for high-speed tensiles; elongation speeds are usually from  $10^{-3}$  to  $10^4$  s $^{-1}$ .

Impact strengths depend on experimental conditions. The smaller the radius of the notch, the higher is the stress concentration at the tip and the lower is the impact strength. At very low temperature, all polymers are brittle. The mobility of chain segments increases with increasing temperature, allowing stresses to be relieved by shear-band or craze formation: impact strengths increase with temperature, especially near the glass transition temperature. Polymers with additional transition temperatures below the glass transition temperatures are for the same reason almost always more impact resistant than polymers without such transitions. Nonentangled polymers exhibit very low impact strengths because no crazes can be formed. The impact behavior of polymers can be improved considerably by modification with rubber (see Section 11.4.3).

#### 8.6.5. Stress Cracking

Stress cracking (stress corrosion, stress crazing) is the formation of crazes under the physical action of chemicals, especially surfactants. Stress corrosion starts at polymer surfaces and proceeds into the interior until the polymer finally cracks. The appearance and the extent of stress cracking depend on the polymer–reagent interaction and the magnitude of the stress.

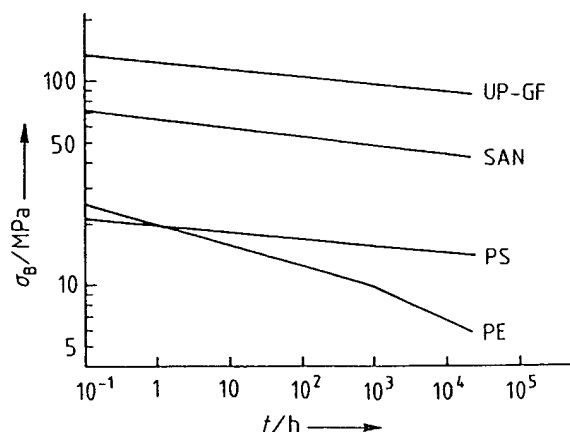
Effects are weak in nonwetting liquids but strong in polymer–liquid systems with solubility parameters of polymers and liquids matching

each other and even more dramatic under tension in the presence of surfactants. Stress cracking decreases with increasing molar mass of the polymer since entanglements allow stresses to relax elastically. Cross-linked polymers are less prone to stress cracking for the same reason. Stress cracking is also reduced if polymer plasticizers are present in plastics because these additives increase the mobility of chain segments and thus the ability to relieve stresses. The same action is responsible for the fact that no stress corrosion is observed above glass transition temperatures.

#### 8.6.6. Fatigue

Materials may be damaged not only “instantaneously” (i.e., on impact) but also by static or periodic loads after certain times or number of loadings. This fatigue is characterized by the *fatigue limit* (endurance) at which the plastics are not damaged even after infinite time and the *fatigue strength*, which indicates the load at which damage sets in after a certain time.

Plastics may be subjected to static loads for certain times  $t$ , after which their fracture strengths  $\sigma_B$  are measured by tensile tests. The logarithms of strength of amorphous polymers usually decrease linearly with logarithms of time due to viscous flow (Fig. 55). Partially crystalline polymers show a bend in these lines after certain times, which indicates a change from tough fracture (short times) to brittle fracture (long times), probably caused by recrystallization phenomena.



**Figure 55.** Time dependence of tensile fracture strengths after static loading during time  $t$ . UP-GF = Glass-fiber-reinforced unsaturated polyester; SAN = Styrene–acrylonitrile copolymer (impact polystyrene); PS = Polystyrene; PE = Polyethylene  
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